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# HgCdTe FABRICATION USING DIRECTED ENERGY TECHNIQUES

ROBERT WOLFSON  
(617) 275-6000 EXT. 256  
ANTON GREENWALD  
(617) 275-6000 EXT. 238

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20. and graphoepitaxial growth of a thin crystalline film, and for pulse annealing high-dose implants in CdTe. This new technology should result in larger, more uniform crystals of HgCdTe than are currently available (and unsuitable) for the proposed application.

Results to date have demonstrated that CdTe films can be deposited at sufficient rates of growth for production, and that CdTe and HgCdTe can be processed without damaging the surface. Preliminary measurement of the physical and electrical properties of the deposited films is expected in the next reporting period.

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## SECTION 1

### REPORT SUMMARY

#### 1.1 PURPOSE

The overall purpose of this research is to produce large-area, single-crystal HgCdTe material for infrared detectors.

#### 1.2 TECHNICAL CONSIDERATIONS

The  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  mixed-crystal system has become the leading intrinsic infrared detector material because of its continuously variable energy gap and its inherently high operating temperature. The compositions of greatest interest are near  $x=0.2$ , which corresponds to the important 8-14  $\mu\text{m}$  atmospheric transmission window. Conventional growth techniques, however, are not capable of meeting the requirements for future mosaic focal-plane applications: viz., uniformity better than 0.003 in composition, minimal vertical band-gap gradients, near-intrinsic purity, freedom from residual stresses and surface defects, size greater than 2 inch, and large-scale production capability. Therefore, a new approach to HgCdTe single crystal production is needed which will satisfy these several constraints.

#### 1.3 GENERAL METHODS

The approach taken is to vapor deposit CdTe films on foreign substrates; to crystallize the films, if necessary, by pulsed electron beam heating; and then to convert the CdTe to single-crystal HgCdTe either by the vapor exchange method or by ion implantation of Hg and Te followed by pulsed electron-beam induced recrystallization. Single-crystal films will be obtained by heteroepitaxy or graphoepitaxy, the former by deposition on suitable single-crystal substrates, and the latter by the melting and crystallization of films on substrate surfaces with artificial relief patterns. Uniformity is assured because the deposition, conversion, and pulsed electron-beam processes are inherently uniform. Vertical gradients are avoided by the use of thin films, as are also residual stresses and undesirable surface morphology. Since the chief potential source of contamination is the substrate, purity can be maintained by exercising normal precautions. Finally, this combined use of vapor transport and pulsed electron-beam technologies imposes no limitations upon crystal area; to the contrary, the approach is admirably suited to scale-up for the high-volume production of large-area HgCdTe detector material.



#### 1.4 TECHNICAL RESULTS AND CONCLUSIONS

The parameter regime for the pulsed electron-beam processing of CdTe and HgCdTe has been identified by analytical modeling and experimentation. For a mean electron energy of approximately 20 keV and a constant pulse width of 100 ns, the fluence lies between  $0.5 \text{ J/cm}^2$  and  $0.8 \text{ J/cm}^2$ . The lower threshold represents the minimum fluence to melt the specimen surface; the upper threshold is the maximum fluence that can be sustained by the material without plastic flow and vaporization - induced cratering. Between these limits, surficial melting occurs without damage to the bulk, the depth of melt increasing monotonically as the fluence is raised. The loss of the more volatile components, Cd and Hg, is restricted to a layer definitely less than 50 nm deep and possibly less than 10 nm deep; the surface can be restored by etching.

The hot-wall vapor deposition apparatus for CdTe is now functional, and films have been deposited on muscovite mica at rates up to  $40 \mu\text{m/h}$ . Substrates for the heteroepitaxial growth of CdTe have been identified: viz., silicon, quartz, and sapphire. In addition, texture-etched silicon surfaces have been replicated for use as graphoepitaxial substrates for CdTe growth.

#### 1.5 IMPLICATIONS FOR FURTHER RESEARCH

The results obtained to date confirm the validity of both the general approach and the detailed program plan. Research during the next six-month period will proceed on schedule, as described in Section 5.

#### 1.6 SIGNIFICANT HARDWARE DEVELOPMENT

A hot-wall vapor deposition apparatus<sup>(1)</sup> for CdTe has been designed and constructed; see Figure 3-2. It comprises an evaporation source and substrate furnace contained within a 12 inch bell jar mounted on a turbomolecular pump by means of a stainless steel transition piece. The transition is equipped with flange attachments to accommodate the high current and high voltage feedthroughs, the thermocouple leads, the vacuum gage tube, and the rotary seal used to operate the evaporation shutter. Also included, but not shown, are power supplies and temperature controllers.

## SECTION 2

### DIRECTED ENERGY PROCESSING ASSESSMENT (TASK 1)

#### 2.1 OBJECTIVE

This task is to assess the directed energy processing of CdTe and HgCdTe, with the objective of establishing a starting point for the development of process parameters. The pulsed electron-beam physics associated with the modification of these materials was modeled using relevant published information and, where necessary, estimates of unavailable thermomechanical data. With the numerical results for guidance, pulse processing experiments were performed to establish the limits of the useful processing regime, namely, those values of beam fluence, for a given mean electron energy, below which there is no melting and above which the surface of the sample is damaged by fragmentation or massive slip. Amorphous CdTe, single-crystal CdTe, and polycrystalline HgCdTe were pulsed and then examined for structure, stoichiometry, and uniformity.

#### 2.2 MATERIAL PARAMETERS

The reason for modeling the pulsed electron-beam physics is twofold: first, to estimate the initial parameters for the start of experimentation, and, second, to guide the design of the experiments by placing a limit on the thickness of the material that can be pulse processed. The usefulness of these numerical calculations, in turn, depends upon the accuracy of the input data. The specimen to be irradiated must be clearly defined in the sense of specifying the atomic composition and the density of each component layer; the several thermal and mechanical parameters that enter into the calculations must be known for each layer as functions of temperature.

A survey of the unclassified literature provided much of the needed input data. However, there is a paucity of information on the high-temperature thermal properties of the CdTe-HgTe system, as well as the absence of a reliable model for estimating the properties of liquid alloys from those of the end members. Further, there is an almost total lack of relevant shock and mechanical-strength data.

Our incomplete knowledge of the material properties of CdTe-HgCdTe mixed crystals restricted meaningful calculation to pure CdTe, to  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ , and to thin Hg films over CdTe. Here, the data were sufficiently detailed to warrant the application of the electron-deposition and the thermal-diffusion programs of the numerical model (see Section 2.3). On the other hand, the hydrodynamic-shock program could not be used with confidence, and empirical bracketing by experiment was substituted for the model (see Section 2.4).

### 2.3 ENERGY TRANSPORT PHENOMENA

The energy transport phenomena induced by the pulsed electron beam are described by a numerical model comprising four calculations. The first, which characterizes the beam by deriving the electron energy spectrum from the diode current and voltage, requires no information on the material being processed. For the present investigation, four beam types were evaluated; they can be differentiated most succinctly on the basis of penetrating capability:

- o The shallow beam, with a mean electron energy  $\leq 15$  keV
- o The low-intermediate beam, with a mean electron energy  $\sim 20$  keV (this beam had been developed specifically for GaAs)
- o The high-intermediate beam, with a mean electron energy  $\sim 35$  keV
- o The deep beam, with a mean electron energy  $\geq 50$  keV

The second calculation uses the electron energy spectrum to estimate the deposition profile in the material; it gives dose (energy/gm/energy/cm<sup>2</sup>) as a function of depth below the specimen surface. The several specimen-beam combinations treated are listed in Table 2-1. The third calculation uses the deposition profile and the fluence to estimate the temperature profile as a function of time; the results are most conveniently expressed as temperature versus depth for various times after the end of the pulse and as temperature versus time for various depths below the surface. On the basis of the preceding deposition profiles, attention was directed towards low electron energies (the shallow and low-intermediate beams) and fluences that are considered moderate for material-processing applications (on the order of 1 J/cm<sup>2</sup>). The fourth calculation, which was not performed because of insufficient data, would have estimated the effect of hydrodynamic shock upon the material.

TABLE 2-1. ELECTRON-DEPOSITION CALCULATIONS

Specimen	Beam	Angle of Incidence
0.05 $\mu\text{m}$ Hg over 19.95 $\mu\text{m}$ CdTe	shallow	0°
0.10 $\mu\text{m}$ Hg over 19.90 $\mu\text{m}$ CdTe	shallow	0°
0.50 $\mu\text{m}$ Hg over 19.50 $\mu\text{m}$ CdTe	shallow	0°
4.24 $\mu\text{m}$ Hg over 27.93 $\mu\text{m}$ CdTe	shallow	0°
6.55 $\mu\text{m}$ Hg over 21.44 $\mu\text{m}$ CdTe	shallow	0°
7.20 $\mu\text{m}$ Hg over 12.80 $\mu\text{m}$ CdTe	shallow	0°
0.05 $\mu\text{m}$ Hg over 19.95 $\mu\text{m}$ CdTe	deep	0°
0.10 $\mu\text{m}$ Hg over 19.90 $\mu\text{m}$ CdTe	deep	0°
0.50 $\mu\text{m}$ Hg over 19.50 $\mu\text{m}$ CdTe	deep	0°
4.24 $\mu\text{m}$ Hg over 27.93 $\mu\text{m}$ CdTe	deep	0°
6.55 $\mu\text{m}$ Hg over 21.44 $\mu\text{m}$ CdTe	deep	0°
7.20 $\mu\text{m}$ Hg over 12.80 $\mu\text{m}$ CdTe	deep	0°
Hg <sub>0.8</sub> Cd <sub>0.2</sub> Te	high-intermediate	0°
Hg <sub>0.8</sub> Cd <sub>0.2</sub> Te	high-intermediate	60°
CdTe	high-intermediate	0°
CdTe	high-intermediate	60°
CdTe	shallow	0°
CdTe	shallow	0°
CdTe	low-intermediate	0°
CdTe	low-intermediate	45°
Cdte	low-intermediate	60°

The results of the numerical modeling for the CdTe-HgTe system show clearly the distinctive features of the four beam types:

- o The shallow beam produces a deposition profile that falls sharply and monotonically from the surface, with the temperature profiles correspondingly abrupt. For fluences near  $1 \text{ J/cm}^2$ , the shallow beam is capable of melting the material to a depth on the order of 0.5 micrometer.
- o The low-intermediate beam yields a deposition profile with its maximum a few tenths of a micrometer below the specimen surface and with a comparatively broad peak. Like the shallow beam, the low-intermediate beam produces surficial melting, but the temperature profiles are considerably less steep.
- o The high-intermediate and deep energy beams deposit their energies at depths that are too great for melting thin surficial layers; indeed, their deposition profiles are characterized by maxima on the order of micrometers below the surface.

The low-intermediate beam, with a mean electron energy  $\sim 20 \text{ keV}$ , was selected for further process development. As shown by the deposition and temperature profiles reproduced as Figures 2-1 and 2-2, it offers the capability of melting thin surface layers with good depth control, which is essential for maintaining uniform composition. Moreover, the subsurface deposition peaks appear to cause little overheating of the molten surface and should thus promote stoichiometry, while the comparatively gentle temperature profiles in the bulk material are expected to minimize the occurrence of damaging thermal stresses. These several observations were corroborated and extended by the pulse-processing experiments described in the following section.

#### 2.4 PULSE-PROCESSING OF HgCdTe and CdTe

Three experiments were performed on bulk material using the low-intermediate beam at  $45^\circ$  incidence.

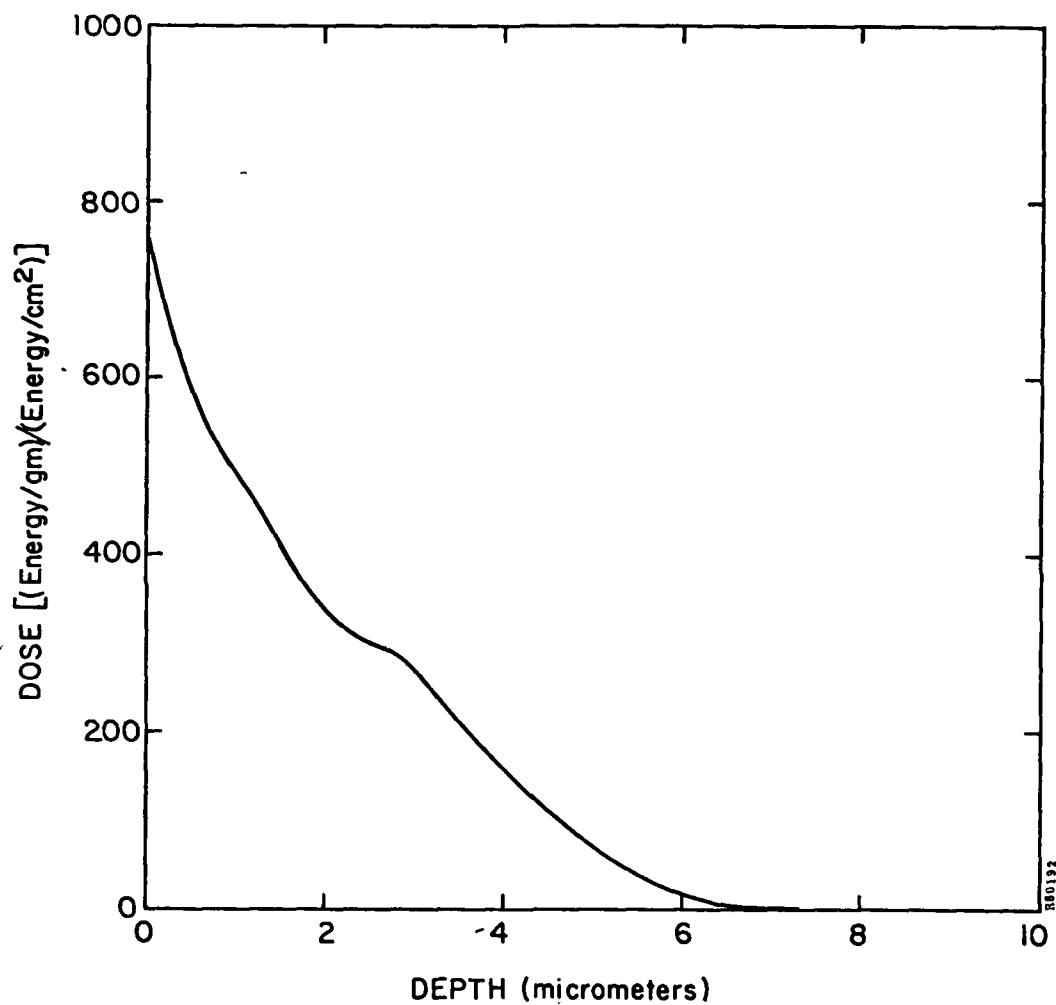


Figure 2-1. Energy deposition profile into CdTe by 20 keV average electron energy beam. (Note that dose, energy/gm, is normalized to a unit fluence, energy/cm<sup>2</sup>.)

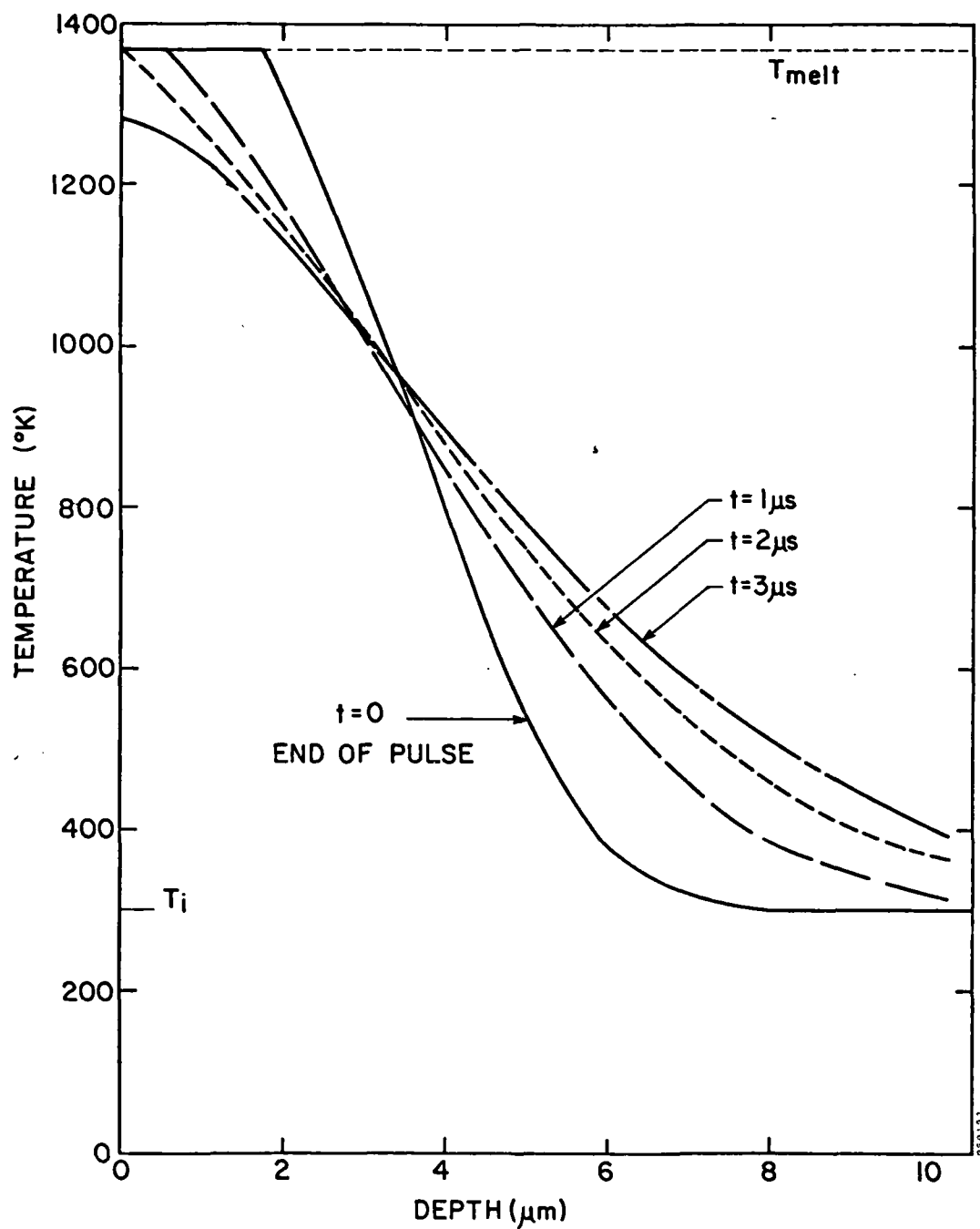


Figure 2-2. Thermal history of CdTe surface pulse heated by electron beam with spectrum shown in Figure 2-1, at  $0.9 \text{ J/cm}^2$ .



- o The first experiment defined the useful processing regime by determining the threshold values of beam fluence for melting and for damaging single-crystal CdTe.
- o The second confirmed that the beam parameters indicated by the first experiment are suitable for pulse-processing CdTe.
- o The third extended the demonstration of useful pulse-processing to  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ .

The CdTe specimens were wafers cut from a single crystal which had been rejected for optical use because of growth twins but which was otherwise judged to be of the highest quality. The wafers are nominally 2 inches in diameter and 0.120 inch (3 mm) thick, polished on one side and lapped on the back. Figure 2-3 is a photograph of the back of one such wafer, showing the typical substructure of large twins with areas of 1-10  $\text{cm}^2$ . All processing was done on the polished surface. The sole specimen of  $\text{HgCdTe}$ , approximately 10  $\text{mm}^2$  in area and 1 mm thick, was cut from a solid-state-recrystallized (SSR) wafer about 0.5 inch across; the latter had been provided by NERC, which stated its nominal composition to be  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ . Specimens were cleaned in successive baths of Alconox, deionized water, trichloroethylene, and methanol prior to use.

#### 2.4.1 Definition of Useful Processing Regime

The first series of experiments determined the minimum fluence required to melt the surface of single-crystal CdTe and the maximum fluence that can be sustained by the material without damage to the bulk. Since the calculations presented in Figure 2-2 indicated that the lower threshold is less than 0.8  $\text{J}/\text{cm}^2$ , the determination started at a fluence of 0.25  $\text{J}/\text{cm}^2$  and moved up in increments of approximately the same magnitude. Structural changes induced by irradiation were detected by examining the polished surface under the optical microscope.

The experimental results are given in Table 2-2. They indicate that single-crystal CdTe can be pulse-processed, i.e., surficially melted, without appreciable damage to the bulk, using a fluence of about 0.50  $\text{J}/\text{cm}^2$ .

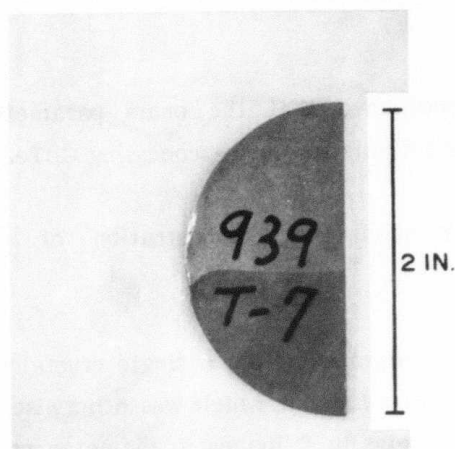


Figure 2-3. Back of CdTe sample wafers showing twinned structure.

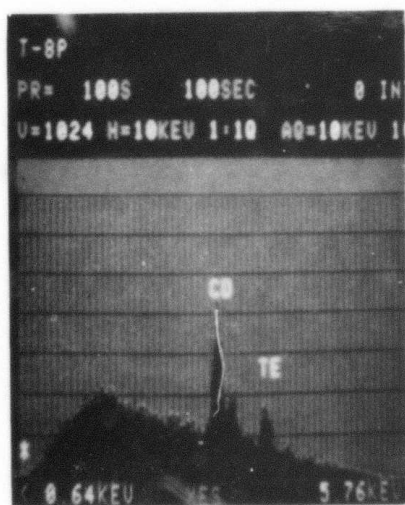


Figure 2-4. Energy dispersive analysis of x-rays (EDAX) of CdTe crystal pulsed at  $0.5\text{J}/\text{cm}^2$ .

TABLE 2-2. PULSE-PROCESSING OF SINGLE-CRYSTAL CdTe;  
LOW-INTERMEDIATE BEAM AT 45°

Fluence J/cm <sup>2</sup>	Surface Appearance After Irradiation	Interpretation
0.25	no change	—
0.50	color change	surface melting; corroborated by SEM, EDAX, Auger spectroscopy
0.81	irregular discoloration; random pitting; a few slip lines	minor plastic flow
1.02	numerous slip lines	large-scale plastic flow
1.05	numerous slip lines	large-scale plastic flow

The wafer irradiated at 0.50 J/cm<sup>2</sup> (wafer T-8) was subsequently cleaved into smaller samples for substantiation of melting and for examination of stoichiometry. Scanning electron microscopy<sup>(2)</sup> revealed clear evidence of surface melting; in situ energy dispersive analysis of x-rays (EDAX) showed some loss of cadmium. See Figure 2-4 (on the preceding page) for the integrated x-ray spectrum and Table 2-3 for the calculated elemental composition.

TABLE 2-3. EDAX ANALYSIS (15 kV BEAM) OF CdTe BEFORE AND AFTER  
PULSE-PROCESSING AT 0.50 J/cm<sup>2</sup>

Element and Precision	Atomic Percent Calculated from X-Ray Spectrum			
	Cd	2Σ	Te	2Σ
Before Pulse-Processing	49.2	1.2	50.8	1.7
After Pulse-Processing	45.7	1.0	54.3	1.4

Since a deviation from stoichiometry was observed, a second sample from this same specimen was submitted for Auger spectroscopy<sup>(3)</sup> with depth profiling by argon ion sputtering. The results, presented as Figure 2-5, confirmed that the pulse-induced melting changes the composition of the surface. In the unpulsed CdTe, surface contamination, principally carbon and oxygen, reduces the signals of the two main constituents, but the identical behavior of their traces indicates constant composition (at 50:50 atomic percent) with depth. In the pulse-processed crystal, on the other hand, the variance between the two signals indicates a drop in cadmium concentration at the surface. The depth of the affected layer is definitely less than 0.5 nm and possibly less than 10 nm; a more exact determination was precluded by the incompletely known dependence of the sputtering rate upon the composition.

The specimens used to locate the threshold for damage were quarter-wafers cut from wafer T-10. The specimen irradiated at  $0.81 \text{ J/cm}^2$  was irregularly discolored and randomly pitted (Figure 2-6a); away from the central region of the Gaussian beam distribution, where the fluence was slightly lower, both pitting and discoloration were reduced (Figure 2-6b). Irradiation at  $1.02 \text{ J/cm}^2$  and at  $1.25 \text{ J/cm}^2$  induced large-scale plastic deformation, as evidenced by the appearance of slip lines on the specimen surfaces (Figure 2-6c); the extent of the deformation seemed greater at the higher fluence.

These results indicate that the middle of the useful processing regime for the low-intermediate beam at  $45^\circ$  incidence corresponds approximately to  $0.6 \text{ J/cm}^2$ , and this fluence was tentatively chosen for further process development.

#### 2.4.2 Pulse-Processing of As-Implanted CdTe

The second experiment confirmed the capability of the selected beam to melt the surface of CdTe and to anneal the radiation damage left by high-dose ion implantation. A CdTe wafer (wafer T-11) was implanted with arsenic at 50 keV to a dose of  $10^{16}$  ions per  $\text{cm}^2$ . Arsenic was used as the implant ion in order to facilitate comparison with the literature on thermal annealing<sup>(4)</sup>; the dose was made high enough to yield an easily measured profile. The implanted wafer was cleaved into quarters, one of which was pulse-processed at the fluence of  $0.6 \text{ J/cm}^2$ . Although analysis is still in progress, ion scattering spectrometry (ISS) has shown that the implanted arsenic was redistributed during irradiation (Figure 2-7), thereby verifying that the surface had indeed been melted.

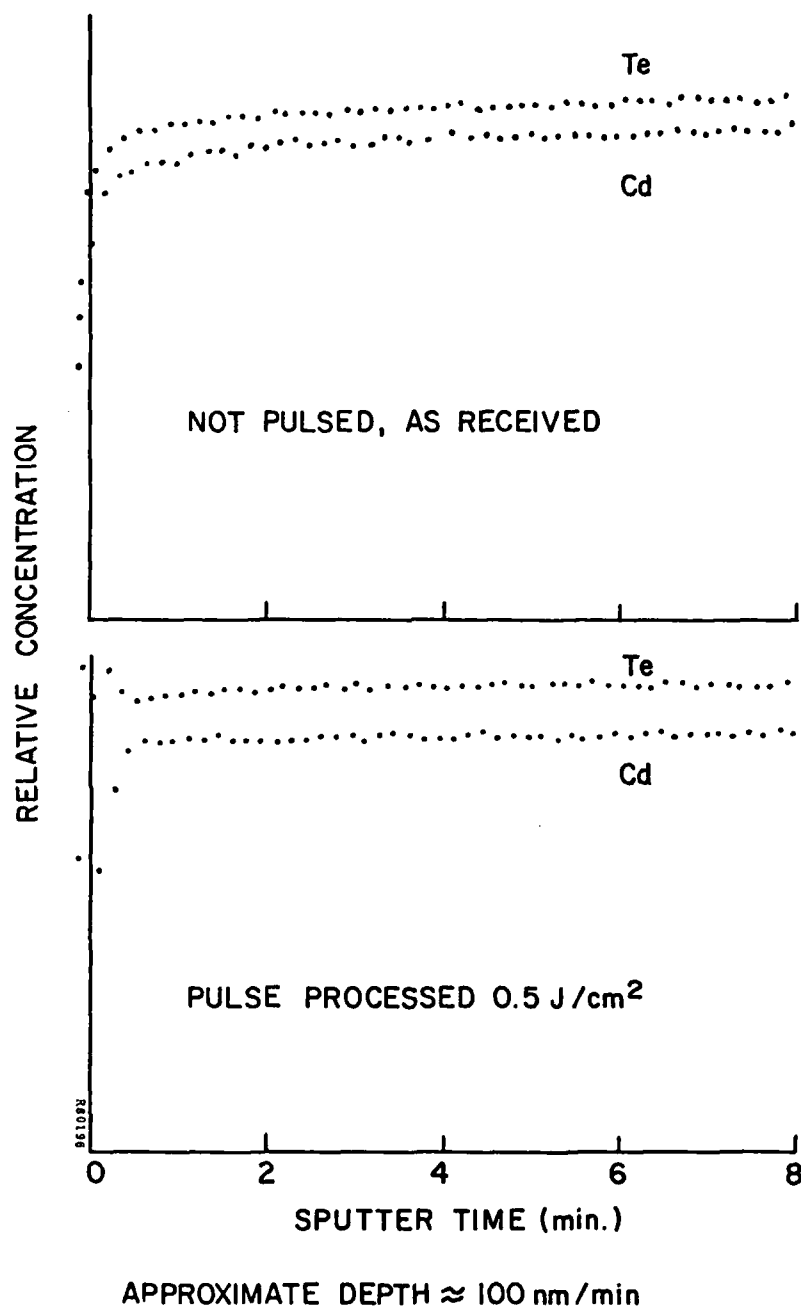
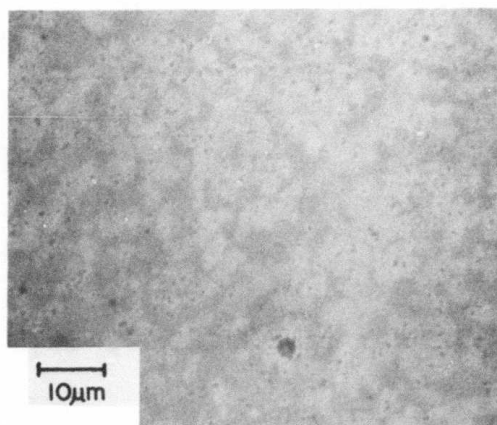


Figure 2-5. Depth profile of Cd and Te by Auger spectroscopy and argon ion sputtering for unprocessed and pulse-processed CdTe crystal at 0.5 J/cm<sup>2</sup>.



(a)



(b)



(c)

Figure 2-6. Photomicrographs (approximately 1000X) of pulse-processed CdTe crystals examined for damage threshold: (a)  $0.8 \text{ J/cm}^2$ , (b) less than  $0.8 \text{ J/cm}^2$  outside region of beam focus, and (c)  $1.25 \text{ J/cm}^2$ .

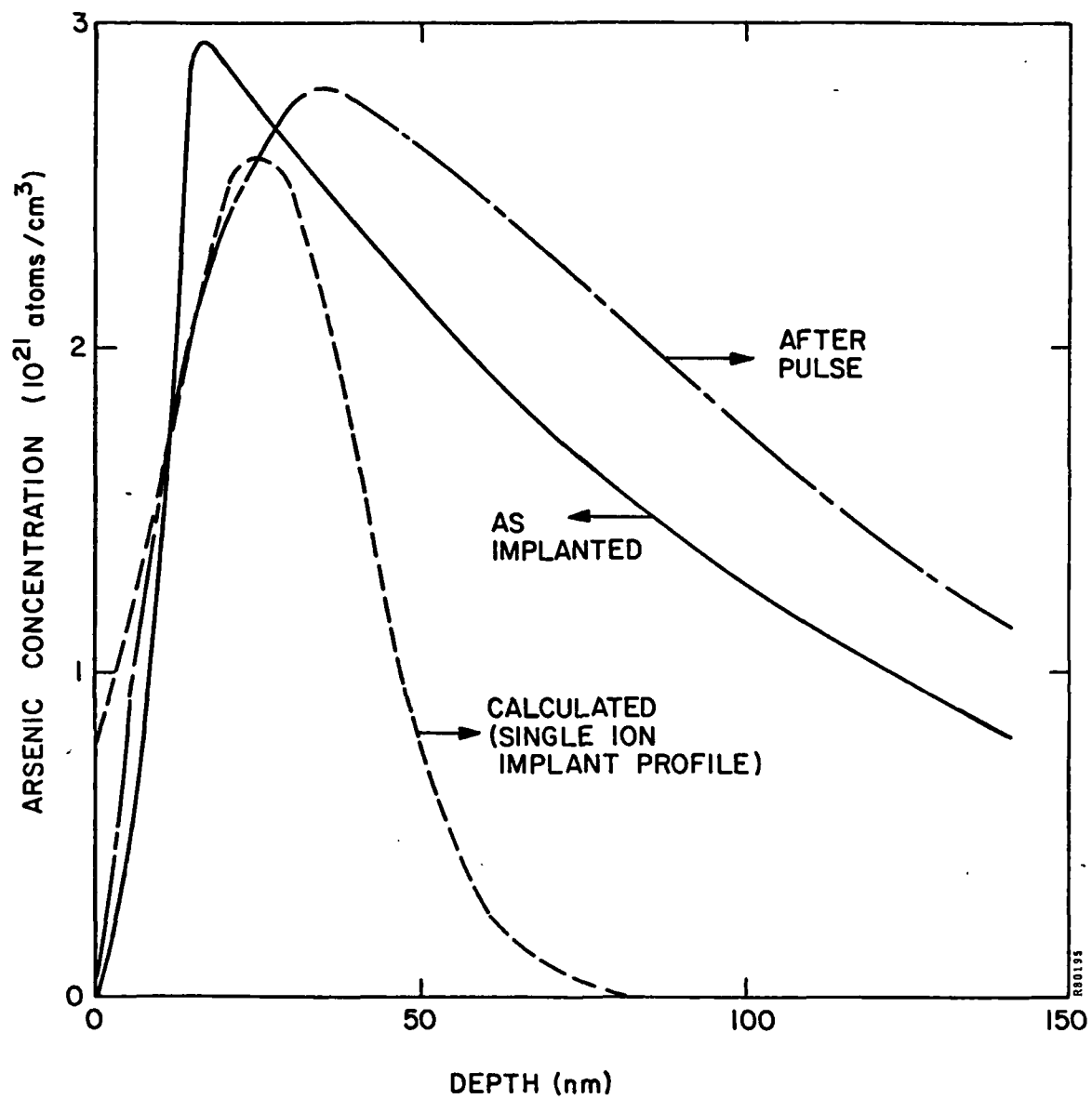


Figure 2-7. Profile of arsenic concentration implanted in CdTe and after pulse-processing at  $0.6 \text{ J/cm}^2$ . (Note: Data by ISS and ion sputtering.)



#### 2.4.3 Pulse-Processing of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$

The third experiment demonstrated that the selected beam is also suitable for processing  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ , which is the desired end-product of the present program. A specimen of polycrystalline SSR-grown material of this composition was irradiated at  $0.60 \text{ J/cm}^2$ . No evidence of damage was found. Auger spectroscopy with ion-sputtering depth profile analysis yields curves (Figure 2-8) which are analogous to those for CdTe (Figure 2-5); namely, the concentrations of cadmium and mercury have been reduced in a thin surficial layer.

#### 2.5 EVALUATION OF PULSE-PROCESSING EFFECTS

The analytical results of physical modeling were used to establish a starting point for the development of process parameters; i.e., the low-intermediate beam (mean electron energy  $\sim 20 \text{ keV}$ ) was identified as the best suited for producing surficial melting with minimal damage, and the angle of incidence was set at  $45^\circ$ . Pulse-processing experiments were then performed with this beam in order to determine proper values of fluence. (The mean electron energy and the fluence are the critical beam parameters, since processing effects are relatively insensitive to the details of the electron energy spectrum and to the pulse width.) The modest goal of these preliminary experiments has been met. A range of fluence has been identified for pulse-processing CdTe, bounded on the low side by no effect and on the high side by unacceptable damage. Between these values, the material may be melted to a variable depth, with a maximum of about one micrometer. The material  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  appears to behave in a similar fashion, and the same limits to pulse-processing have been applied.

The experiments show that the more volatile components, Cd and Hg, are lost from a thin surface layer believed to be less than 50 nm thick. Experience with processing GaAs has shown that good surface characteristics can be recovered by etching to remove the excess component.<sup>(5)</sup> Alternately, a cap of  $\text{Si}_3\text{N}_4$  or similar material may be used<sup>(6)</sup> to retain good surface quality. The change in surface composition is restricted and not expected to be a problem.

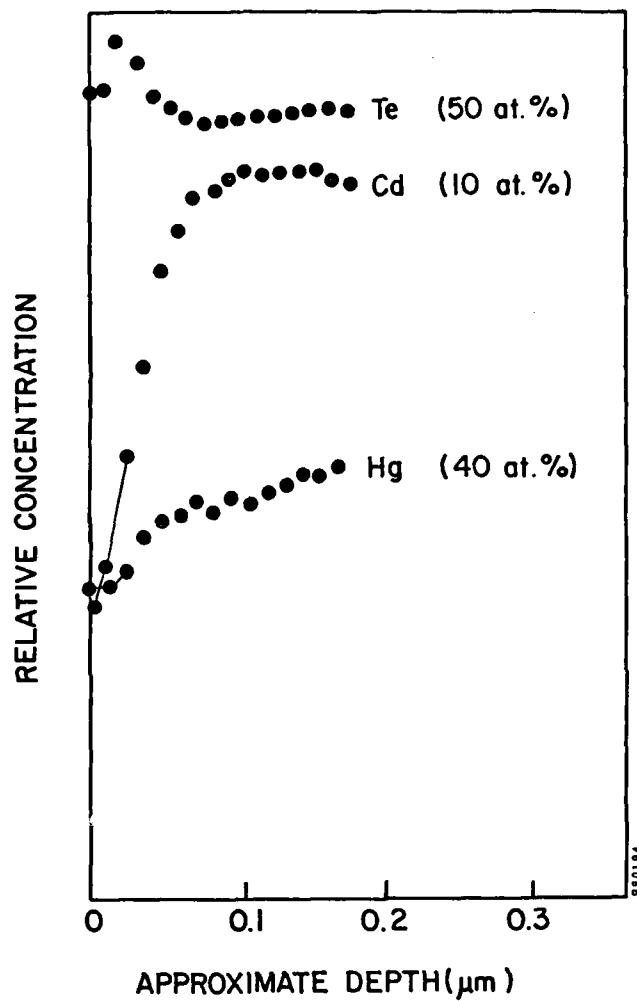


Figure 2-8. Depth profile of Hg, Cd, and Te in pulse-processed  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  at  $0.6 \text{ J/cm}^2$ . (Note: Data by Auger spectroscopy and ion sputtering.)

SECTION 3  
FABRICATION OF SINGLE-CRYSTAL CdTe FILMS  
UPON FOREIGN SUBSTRATES (TASK 2)

3.1 OBJECTIVE

This task is to fabricate the single-crystal CdTe films required by the vapor exchange method (Task 2) for producing HgCdTe of infrared-detector quality. CdTe films of various thicknesses are to be evaporated onto substrates chosen for their suitability as mechanical supports and as nucleating surfaces; artificial surface structure for graphoepitaxy will be considered, in addition to conventional structure matching for heteroepitaxy. The films, presumably polycrystalline or even amorphous in the as-deposited condition, are to be pulse-processed in order to induce large-area, high-quality crystal growth. They are to be thoroughly characterized.

The task is divided into the following subtasks:

1. Substrate Considerations
2. Substrate Selection
3. Apparatus Design and Setup
4. Process Definition
5. Vapor Deposition of CdTe Films
6. Pulse Crystallization
7. Film Characterization

The present report covers subtasks 1 through 3.

3.2 SUBSTRATE CONSIDERATIONS

There are two alternative phenomena that can be used to produce single-crystal films on foreign substrates: heteroepitaxy and graphoepitaxy. Heteroepitaxy obtains when the crystallographic orientation of the substrate uniquely determines the orientation of the deposited film. Thus, a single-crystal substrate induces the growth of a single-crystal layer, although the two may have totally different crystal structures, e.g., (111) silicon on (0001) sapphire. The theoretical explanation of heteroepitaxy is

not complete, but its occurrence is known to be promoted by close structural matching, viz., low volume misfit and compatible symmetries across the interface plane. In addition, since structural control is exerted primarily by atomic interactions during film nucleation, the substrate surface must be truly clean, a condition commonly achieved by in situ vapor etching. Graphoepitaxy, by contrast, induces single-crystallinity by means of artificial relief features on the substrate surface which constrain crystallite growth during film solidification. In graphoepitaxy, the atomic structure of the substrate is irrelevant and can even be amorphous.

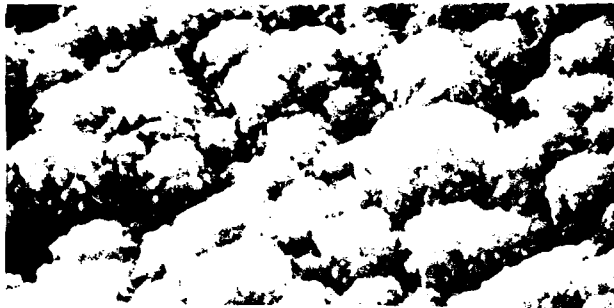
The heteroepitaxial growth of CdTe and HgCdTe has been the subject of numerous investigations. Deposition techniques<sup>(1, 7-11)</sup> have included chemical vapor deposition, evaporation, and sputtering; substrates have ranged from other compound semiconductors<sup>(11)</sup> to silicon,<sup>(1)</sup> sapphire,<sup>(8)</sup> muscovite mica,<sup>(1)</sup> and various alkali halides.<sup>(9)</sup> The best films obtained to date have been heavily twinned single crystals, the twinning presumably due to the high degree of pseudosymmetry inherent in the zinc blende structure. Therefore, although the choice of substrate can influence the density of twins, it cannot be expected to eliminate them completely.

Heteroepitaxy is to be the principal approach for this program. We propose to improve upon current heteroepitaxial techniques by pulse processing: specifically, by melting the thin (0.1-1.0  $\mu\text{m}$ ) film with only minimal heating of the substrate. The very large thermal gradient established upon cooling will result in strictly unidirectional solidification, which should suppress the growth of twins. There will be some loss of cadmium from the surface, to a depth of perhaps 50 nm, but this is expected to be no more serious than the similar loss of arsenic from pulse-processed GaAs.<sup>(5)</sup>

Graphoepitaxy is to be a secondary approach for fabricating single-crystal CdTe films upon foreign substrates. Although the artificial surface pattern used to induce single-crystal growth is wholly unrelated to the crystal structure of the epitaxial layer, the cross-sectional profile of the grating is both specific and critical, namely, achieving the correct angles between the facets and maintaining a very small radius of curvature at re-entrant corners. We propose to circumvent the difficulties inherent in the preparation of the surface-relief grating by using the two-dimensional pattern produced by the preferential etching of a single-crystal surface. (The two most obvious candidates are silicon and CdTe). The etched surface can be replicated without loss of significant detail (Figure 3-1), using a material suitable for the deposition and pulse-processing of the CdTe film.



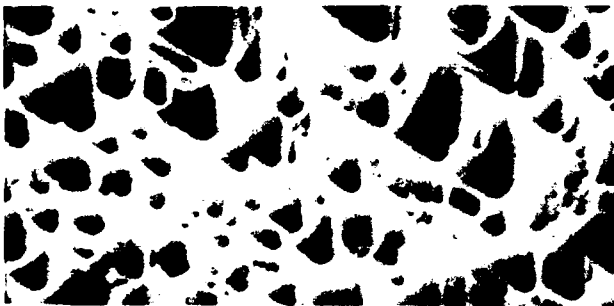
Texture-Etched  $\langle 100 \rangle$   
Si Surface  
x5000



Surface Coated  
with 1 micron Al  
x5000



Si Surface After  
Al Liftoff  
x5000



Al Replicate of  
Texture-Etched  
Surface  
x5000

R79053P

Figure 3-1. Substrate preparation for graphoepitaxy approach to the formation of thin, single crystal CdTe films.

### 3.3 SUBSTRATE SELECTION

Heteroepitaxy and graphoepitaxy impose very similar constraints upon the nature of the substrate, despite the fundamental difference between the two phenomena. The important characteristics for evaluating potential substrate materials are as follows:

1. Capability to induce single-crystal growth in the desired orientation
2. Compatibility with deposition process
3. Thermal expansion coefficient
4. Availability
5. Cost
6. Compatibility with mosaic array experiments

Only the first of these six considerations need be specialized for the two cases. For heteroepitaxy, the primary constraint is that the crystal structure of the substrate be a good match to that of the film in lattice spacing and symmetry. For graphoepitaxy, it is that the material properties of the substrate be suitable for the preparation of the surface-relief pattern. The second requirement means simply that the substrate cannot react with or contaminate CdTe or HgCdTe. (A moderate electrical conductivity would be preferred for pulse-processing, but this is not essential.) The third requirement is that the thermal expansion coefficient of the substrate must match that of CdTe over a wide temperature range (77°K to melt). The material will be deposited at approximately 400°C; pulse-processing will raise the temperature to over 1400°C; and operation of detectors is usually at liquid-nitrogen temperature for very long wavelength devices. Any substantial mismatch in thermal expansion will damage the film. The last three characteristics are for future requirements, except that relatively inexpensive material would be chosen to test processing equipment.

For test purposes, muscovite mica will be used. It is inexpensive, and clean surfaces can be obtained easily by cleaving. It is suitable for testing the deposition parameters of the system. For later use crystalline sapphire cut perpendicular to the c-axis might be used, since it is fairly close to HCT in thermal expansion coefficient. For large-size substrates crystalline quartz and silicon have points in their favor. The plan is to try numerous substrates at the beginning and to home in on a few during the course of the program.

For the graphoepitaxial approach, silicon can be easily etched (Figure 3-1). A replica can be made in aluminum or the surface covered with oxide. An attempt will be made to duplicate this etched pattern in CdTe, but no further work is planned on this approach until after analysis of samples from the heteroepitaxial approach.

### 3.4 APPARATUS

The method most successfully used to date for the vacuum deposition of heteroepitaxial films of CdTe<sup>(1)</sup> is that of the "hot wall" furnace. In hot wall epitaxy the entire channel from the source to the substrate is heated to prevent the depletion of the higher vapor pressure element.<sup>(12)</sup> In most experiments reported, the sample and substrate are maintained at the same temperature (isothermal growth). The effect of a temperature gradient has been investigated.<sup>(7)</sup> The rate of growth can be controlled with the additional variable, but imposing a thermal gradient did not yield better films.

The evaporation source constructed for this program is shown in Figure 3-2. The substrate and CdTe source are in separately controlled furnaces, and the entire system is almost closed, so that the higher vapor pressure component (Cd) is not depleted and growth is in quasi-equilibrium conditions. The maintenance of strict purity control is essential in this furnace, where the weight ratio of the epitaxial film to its container will be very low. Therefore it was decided to operate the vacuum system in the  $10^{-8}$  torr range and dedicate the system to deposition of CdTe films.

During this report period the vacuum system and source for deposition of high purity CdTe films was constructed and tested.

The system was pumped by means of a Welch Model 3102 Turbomolecular Pump backed by a Welch Model 1397 Mechanical Pump. The turbomolecular pump was connected to a 12" bell jar by means of a stainless steel transition (see Figure 3-2). The transition had eight Varian 2" Conflat flange attachments, which are used for the following purposes:

1. One high current electrode
2. Two high current electrodes
3. Eight electrical connectors for thermocouples
4. One high voltage feedthrough



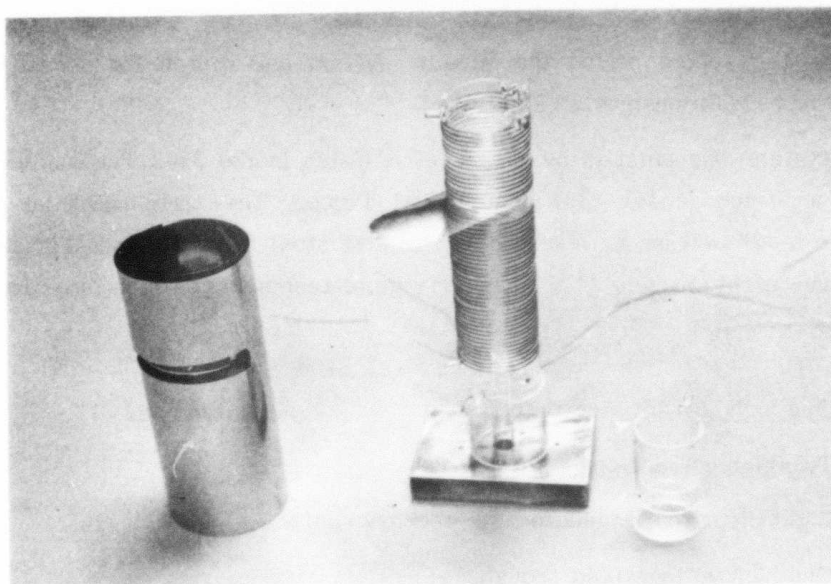
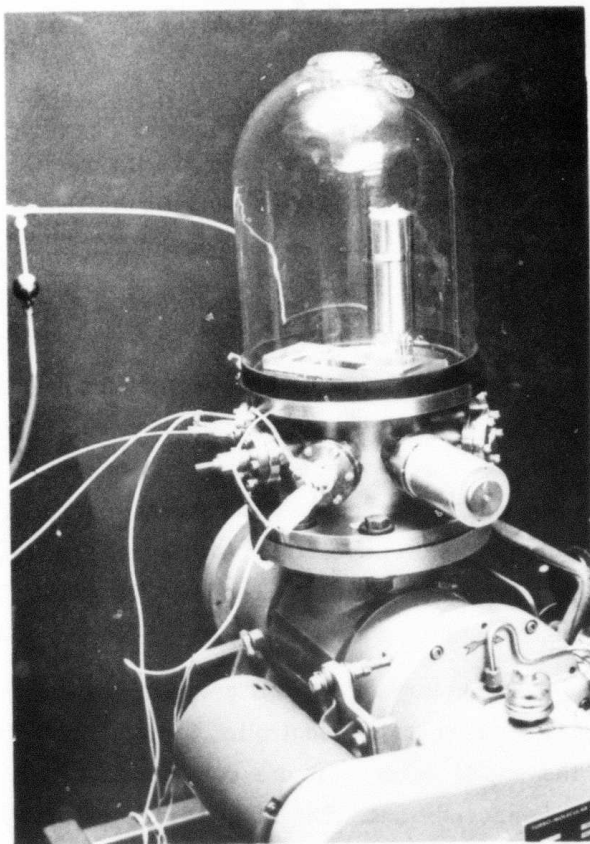


Figure 3-2. Apparatus for the deposition of CdTe films: (top) furnace mounted in bell jar on vacuum pump; (bottom) detail of furnace with shutter and heat shield.

5. Ion gage tube and dry nitrogen input
6. Rotary seal
7. Blank flange for possible future use
8. Blank flange

The three high current feedthroughs allow us to have three separate furnaces.

The high voltage feedthrough allows for the possibility of glow discharge substrate cleaning at a later date. The low current connectors are sufficient to allow the use of four thermocouples. The vacuum gage tube is of the Bayerd Alpert type, and when used with its Granville Philips 412 Ionization Gage Control, allows the measurement of pressures down to the  $10^{-9}$  torr range. The rotary seal will be used to operate a shutter within the system, to prevent deposition of the CdTe film until the pressure and the temperature of the source and substrate furnaces are stabilized.

The glass bell jar was connected to the stainless steel transition by an L-shaped Viton gasket. A nitrogen trap was formed by an indentation 4 inches deep on top of the bell jar. This allows for the convenient trapping of condensibles in the bell jar.

The initial plan was to put an 8 inch gate valve between the turbomolecular pump and the transition to enable the bell jar to be isolated from the pumping system so that the pumps could be kept running and valved off from the bell jar when the bell jar was reloaded. We found, however, that the time gained by this procedure was more than offset by the outgassing problem of the inner surfaces of the gate valve, and thus the valve was discarded.

The system was leak checked by means of an NRC leak detector and attained the  $10^{-8}$  torr range with nitrogen in the trap. The vacuum is limited by the O-ring connections between pump, transition, and bell jar. Improvement would call for metal seals, but the expense and large increase of cycling time involved in this refinement are not justified at this time.

The evaporation source and substrate furnaces (Figure 3-2) were fabricated from a single 125 mm length of 34 mm i.d. quartz tubing. The surface was grooved by two spirals on a 13 per inch thread pitch. These grooves serve to hold the molybdenum wire used for the furnaces. The source furnace is 60 mm long and the substrate furnace 35 mm long. A slit is formed half-way through the tube between the furnaces, so that a shutter may be inserted to separate the source from the substrate. The source is placed

on a platform which is pierced by the source thermocouple tube, and the substrate is supported by a quartz support ring which is fused to the middle of the substrate holder module. The twin furnace is surrounded by two layers of stainless steel for radiation shielding.

A number of calibration runs have been made using this source and system. In all cases the substrates have been freshly cleaved mica, and film thicknesses have been measured by weighing the mica, before and after deposition of the CdTe film. Mica substrates were used for calibration runs because they are cheap and because they are easy to produce in clean form by means of cleaving just before use. When the system calibration runs are complete, silicon and quartz or sapphire substrates will be used. It soon became clear that it is difficult to measure the true temperature of the substrate for two reasons. The temperature of the substrate thermocouple tended to be lower than its surrounding because of radiant losses. This effect is minimized by the addition of a radiation shield over the top of the furnace as well as around the sides. Also, since the mica substrates have poor thermal conductivity, the deposition face is believed to be at higher temperature than the substrate furnace. This is so because the sample faces the higher temperature of the source furnace and the thermal radiation from this furnace raises the temperature of the substrate surface. This effect was minimized by positioning a radiation baffle between the substrate and the source furnace. The baffle was, of course, arranged so that the Cd and Te vapor could freely pass it.

Table 3-1 shows the initial deposition rates measured at various substrate and source temperatures. It is clear that small differences of temperature make a great difference to the rate of film deposition. Numerous runs must be made to determine the optimum values of  $T_{\text{source}}$  and  $T_{\text{substrate}}$  and also to determine the reproducibility of the runs.

TABLE 3-1. DEPOSITION RATE AS A FUNCTION OF TEMPERATURE

Substrate Furnace Temperature (°C)	Source Furnace Temperature (°C)	Deposition Rate $\mu\text{m/h}$
400	550	40
355	513	2.7
327	417	0.07

## SECTION 4

### CONCLUSIONS

Analytical modeling identified the pulsed electron beam with  $\sim 20$  keV mean electron energy, 100 ns pulse width, and  $45^\circ$  angle of incidence as the best suited for processing CdTe and HgCdTe. Experiments with this beam on single-crystal CdTe determined that the minimum fluence for melting the surface is  $\geq 0.5 \text{ J/cm}^2$  and that the maximum fluence sustained by the material without plastic flow and cratering is  $\leq 0.8 \text{ J/cm}^2$ . Within this range, the depth of melt increases monotonically with increasing fluence. Additional experiments on amorphous (arsenic-implanted) CdTe and polycrystalline  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  confirmed that, between these limits, surficial melting occurs without damage to the bulk. In all cases, the surface cools rapidly, and the loss of Cd and Hg is restricted to a layer definitely less than 50 nm deep and possibly less than 10 nm deep. The surface can be restored by etching to remove the excess component.

The hot-wall evaporation furnace for depositing CdTe films has been designed and fabricated. Calibration runs revealed that small differences in the temperatures of source and substrate produce large changes in the rate of CdTe deposition, from  $0.07 \mu\text{m/h}$  with the source at  $417^\circ\text{C}$  and the substrate at  $327^\circ\text{C}$  up to  $40 \mu\text{m/h}$  with the source at  $550^\circ\text{C}$  and the substrate at  $400^\circ\text{C}$ . Although preliminary depositions are to be made, for convenience and economy, on muscovite mica cleavages, substrates for heteroepitaxial growth have been identified and will be used in future work, viz., silicon, quartz, and sapphire. In addition, texture-etched silicon and CdTe surfaces are to be replicated for use as graphoepitaxial substrates.

## SECTION 5

### PLANS FOR NEXT PERIOD

#### 5.1 DIRECTED-ENERGY PROCESSING ASSESSMENT

The ongoing analysis of pulsed samples of CdTe and HgCdTe will be expanded to include characterization of the microstructure, in order to pinpoint the optimum fluence for melting thin layers (less than 1  $\mu\text{m}$  thick). Since the melt depth is now limited by the generation of thermal stresses, which induce plastic flow, the use of moderate substrate temperatures to delay the onset of deformation will be explored. A sample heater is available on the pulsed electron-beam apparatus, and the effect of temperatures on the order of 100°C will be tested. In addition, the potential difficulty in pulse-processing specimens on insulating substrates will be approached by filling the sample chamber with an inert gas, such as argon, at low pressure; the gas will be ionized by the electron beam, and the resultant plasma will carry away the excess charge which might otherwise accumulate.

#### 5.2 FABRICATION OF SINGLE CRYSTAL CdTe FILMS UPON FOREIGN SUBSTRATES

The empirical calibration of the hot-wall evaporation apparatus will be completed; sample CdTe films will then be deposited on mica and characterized for composition and microstructure. After this preliminary process definition, CdTe films of various thicknesses will be deposited upon substrates selected for their capability to induce graphoepitaxial and/or heteroepitaxial growth. These films will be pulse-processed to achieve large-area, high-quality crystal growth and will be thoroughly characterized.

#### 5.3 VAPOR EXCHANGE OF CdTe TO FORM HgCdTe

The design and fabrication of the apparatus to convert the processed CdTe films to HgCdTe will be completed. The process parameters for the conversion of the thin film by vapor transport will be established.

#### 5.4 MODIFICATION OF CdTe BY ION IMPLANTATION TO FORM HgCdTe

The Hg ion source for the ion implanter, already on hand, will be tested. Initially, CdTe films will be implanted at 50 keV and  $10^{15}$ ,  $10^{16}$ , and  $10^{17}$  atoms/cm<sup>2</sup>; samples will be pulse-processed and analyzed for composition and microstructure. Before the end of the half-year reporting period, process definition will have been completed, and ion implantation and pulse-processing for HgCdTe fabrication will be in progress.

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